

REMARKS

The Official Action of 29 August 2007 has been carefully considered and reconsideration and further examination of the application in view of the following amendments and remarks is respectfully requested.

The claims have been amended more clearly to define the subject matter which Applicants regard as their invention without narrowing the scope thereof. The amendments remove the bases for the rejections under 35 U.S.C. §112, second paragraph.

Claims 1, 4, and 14 stand rejected under 35 U.S.C. §103(a) as allegedly being obvious over Tetzlaff et al. (U.S. Pat. No. 5,656,389) in view of Divisek (WO01/61776; U.S. Pat. No. 7,056,610 (relied upon for translation)). The remaining claims stand rejected as allegedly being obvious over Tetzlaff in view of Divisek in further view of the references cited at paragraphs 12-23 of the Official Action. Applicants respectfully traverse the rejections.

The claimed invention is based at least in part on Applicants' discovery that a problem in the alcohol-air fuel cells (AAFC) of the prior art relating to the diffusion of alcohol through an electrolyte membrane to a cathode can be solved with the use of a liquid electrolyte comprising an aqueous alkaline solution. The problem, as discussed in the specification on page 1, lines 14-17, is the presence of significant diffusion of alcohol through

the electrolyte membrane to the cathode that reduces the efficiency of operation of the AAFC and reduces its service life (specification at page 1, lines 14-17).

As explained in the closest prior art reference, Kordesch et al WO 01/39307 (copy submitted herewith), which is cited in the present specification at page 1, lines 18-25, the problem is peculiar to “direct” fuel cells wherein alcohol fuel is introduced directly into the fuel cell (as opposed, for example, to hydrogen fuel cells wherein hydrogen in gaseous state is introduced). The electrolyte membrane of the direct fuel cell must perform a dual function: (a) aiding in conducting protons toward the cathode while (b) preventing fuel from directly contacting the cathode. Unfortunately, known electrolyte membranes are not very efficient as fuel processors resulting in fuel cross over (see Kordesch at paragraph bridging pages 2-3). Kordesch attempted to solve the problem by the provision of an electrolyte chamber comprising a **liquid acid**, which serves to remove any un-oxidized fuel that diffuses through the anode (Kordesch at page 4, lines 19-23). As described in Kordesch, the prior art believed it was necessary to use a liquid acid so as not to hamper the flow of protons to the cathode. See Kordesch at page 6, lines 19-20 (“However, **being acidic**, the fluid electrolyte does not impede the flow of protons between the anode and the cathode.”)

As discussed in the present specification at page 1, lines 22-25, a drawback of the prior art AAFC is that the use of a corrosive acid electrolyte makes the construction of the AAFC more expensive because of the limited choice of structural materials and the necessity to use noble metal catalysts. Applicants have discovered that an efficient direct alcohol air

fuel cell can employ an alkaline liquid electrolyte whereby to avoid this drawback and to enable the use of a non-platinum catalyst. As exemplified in the specification at pages 5-6, the claimed AAFC comprising an alkaline liquid electrolyte can surprisingly develop a current density of at least 80 mA/cm² at a voltage of 0.5V and a temperature of 70°C.

The primary reference cited by the Examiner, Tezlaff et al, does not address the problem faced in the prior art of preventing fuel cross over between the anode and the cathode in a direct AAFC while not impeding a flow of protons between the anode and the cathode. Indeed, as acknowledged by the Examiner, Tezlaff et al describe an electrochemical cell with a gas diffusion cathode and a gas diffusion anode. Both the cathode and the anode make use of gaseous reagents. Tezlaff et al do not show a direct fuel cell wherein an alcohol fuel is introduced directly in the fuel cell nor do they describe an electrochemical cell involving a flow of protons between the anode and the cathode. (Tezlaff et al describe cells involving the flow of OH⁻ and H₂O.) There is thus nothing in Tezlaff et al that would overcome the prejudice of the prior art (see discussion above), and provide even a reasonable expectation of success with the claimed direct AAFC fuel cell comprising an alkaline liquid electrolyte.

Similarly, none of the other references teach the use of an alkaline liquid electrolyte in a direct AAFC fuel cell as claimed whereby none of the other references can overcome the prejudice of the prior art and provide even a reasonable expectation of success with the fuel

cell as defined in any of the claims of record. In the absence of even a reasonable expectation of success, the references cannot set forth even a *prima facie* case of obviousness for the invention as claimed. See MPEP 2143.02 (“Reasonable Expectation of Success is Required”). Put another way, in light of the prejudice of the prior art, there would have been no motivation or reason for one of skill in the art to introduce a liquid alcohol fuel directly into an electrochemical cell, such as described in Tetzlaff, comprising a liquid alkaline electrolyte.

Claim 4 is additionally patentable over these references because it requires that the membrane electrolyte be an anion-exchange membrane. Tetzlaff teaches away from the use of an anion exchange membrane, suggesting that a cation exchanger membrane provides better stability (see column 2, lines 10-13).

Claims 2 and 3 are additionally patentable because claim 2 requires that the membrane electrolyte be a porous matrix impregnated with alkaline electrolyte, and claim 3 requires that the porous matrix be an asbestos matrix. The Examiner contends that Zaromb discloses the asbestos porous matrix and that it would have been obvious to replace the ion exchange membrane of Tetzlaff with the asbestos matrix of Zaromb because the separators are art recognized equivalents. However, Zaromb applies to water-consuming, hydrogen-producing alkaline batteries, and does not consider the proper membrane electrolyte needed for a water-producing DMFC.

Claim 5 is additionally patentable because it requires that the anion-exchange membrane be polybenzimidazole (PBI), doped with OH ions. The Examiner contends that Kerres teaches polyetheretherketone (PEEK) as an art recognized equivalent of PBI because both are listed as preferred thermoplastic backbones for anion-exchange polymers. However, the mere fact that the components at issue are functional or mechanical equivalents does not render them art-recognized equivalents to support an obviousness rejection. *In re Ruff*, 256 F.2d 590, 118 USPQ 340 (CCPA 1958); *Smith v. Hayashi*, 209 USPQ 754 (Bd. of Pat. Inter. 1980). Kerres teaches PEEK and PBI are interchangeable as thermoplastic backbones of an ion-exchange polymer, whether cationic or anionic, when it is combined with or modified by certain ion-exchange groups (see column 6, lines 5-7 and 26-29). It does not follow that PEEK and PBI are interchangeable for all anion-exchange membranes, particularly with regard to the characteristic of resistance to diffusion of alcohol. The present application discloses that PBI, doped with OH has the necessary alcohol diffusion resistance and conductivity (see page 2, lines 22-23). Kerres does not disclose that membranes composed of anion-impregnated PEEK have similar resistance to diffusion of alcohol as anion-impregnated PBI.

Claim 6 is additionally patentable because it requires the cathode to have a hydrophilic barrier layer adjacent the electrolyte chamber. The Examiner contends that the blocking layer used by Tosco to prevent the escape of aqueous electrolyte through the electrode corresponds to the barrier layer of the claimed invention. However, the blocking layer of Tosco is hydrophobic (column 4, lines 33-36), while the barrier layer of the present

invention is hydrophilic. Accordingly, Tosco does not disclose the missing feature of the hydrophilic barrier layer. The Examiner has respectfully not articulated a basis with rational underpinning for rejecting this claim.

Claim 7 is additionally patentable because it requires the cathode to have a hydrophilic barrier layer adjacent the air chamber. The Examiner contends that Yeager discloses the hydrophilic barrier of the claimed invention by reference to a gas carrier layer which defines the gas contacting surface. However, the gas carrier layer of Yeager is hydrophobic (see column 5, lines 47-52 and column 6, lines 29-34), while the barrier layer of the present invention is hydrophilic. Accordingly, Yeager does not disclose the missing feature of the hydrophilic barrier layer. The Examiner has respectfully not articulated a basis with rational underpinning for rejecting the claim.

Claims 8 and 10 are additionally patentable because both require the anode to have an active layer of 3 - 7 wt. % fluoroplastic. Claim 8 further requires the active layer of the anode to have a PBI membrane. Claim 10 further requires the anode to have a porous nickel band filled with PBI. The Examiner contends that Ovshinsky discloses use of the requisite weight percentage of fluoroplastic in the anode. However, Ovshinsky does not disclose the requisite weight percentage of fluoroplastic on the active layer of the anode. Ovshinsky teaches use of a certain weight percentage of polytetrafluoroethylene (PTFE) as a binder on the anode, with additional PTFE for preventing leakage of electrolyte or hydrogen gas (column 10, lines 54-60). Where the anode has multiple layers, Ovshinsky teaches that

the PTFE is disposed on a layer separate from the active layer (column 10, line 66 to column 11, line 7). Accordingly, the PTFE in Ovshinsky is not used on the active layer of the multi-layered anode.

Also, as discussed with regard to claim 5 above, Kerres does not teach the interchangeability of PEEK and PBI for all ion-exchange membranes, particularly with regard to the resistance to alcohol diffusion.

Claim 9 is additionally patentable because it requires that the anode consist of an active layer of 3 - 7 wt. % of PBI and a membrane of PBI. The Examiner contends that Koschany discloses that PEEK is a functional, art-recognized equivalent of PBI, and that it would have been obvious to replace the electrolytic membrane with a PBI membrane. As discussed above, the mere fact that an element is a functional equivalent does not show that it is an art recognized equivalent. Moreover, the use of a thermoplastic as a binder does not disclose that substance as disposed on the active layer of the anode. Even further, Koschany applies only to gas diffusion electrodes, which operate under different principles than the liquid alcohol fueled anode of the claimed invention.

Claim 11 is additionally patentable because it requires that the anode consist of a porous nickel band filled with PBI and an active layer comprising 2 - 7 wt. % of PBI. As discussed above, Koschany does not teach that PEEK is the functional equivalent of PEEK other than potentially as a binder, and it applies only to gas diffusion electrodes. Ovshinsky

does not teach the addition of PBI to the porous nickel band.

Claim 12 is additionally patentable because it requires that the anode consist of PBI-impregnated asbestos and an active layer of 3 - 7 wt. % of fluoroplastic and 2 - 7 wt. % of PBI. The Examiner contends that Zaromb discloses the porous asbestos matrix and Koschany discloses PEEK and PBI as equivalent binder materials. Zaromb applies a different principle of operation, utilizes asbestos for a different purpose, and teaches away from the porosity of the asbestos. Also, as discussed above, Koschany does not teach that PEEK and PBI are art recognized equivalents on the active layer of the anode.

Claim 13 is additionally patentable because it requires the anode catalyst to be a nickel-ruthenium alloy system. Since platinum is not claimed as part of the alloys of claim 13, 20, or 21, the combination of Biberbach and Richter would not yield the nickel-ruthenium alloys of these claims. Claims 22 and 23 do not comprise the simple combination of a platinum ruthenium alloy with a nickel aluminum or nickel aluminum molybdenum alloy since the claimed combination is itself an alloy rather than the simple mixture of the prior art compositions. The specific weight percentages of platinum and ruthenium as claimed in claim 24 are not disclosed in either reference.

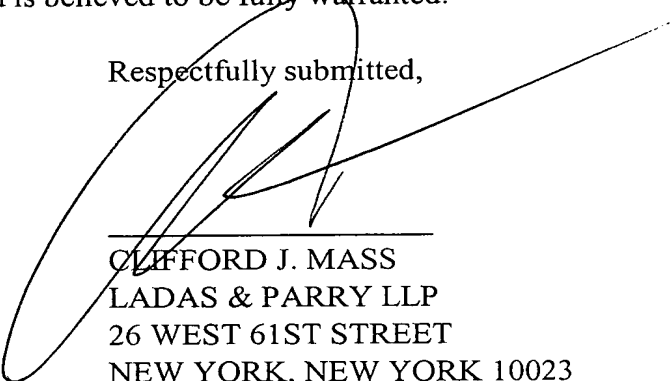
Claim 26 is additionally patentable because it requires the claimed three layer structure. Moreover, as discussed previously, Kerres does not teach that PBI and PEEK are interchangeable as membrane ion-exchangers and Biberbach and Richter cannot be

combined to arrive at a nickel ruthenium catalyst without platinum, molybdenum, and aluminum also within the alloy.

Claim 19 is additionally patentable because it requires that the carbon carrier be carbon black or graphite with specific surface area of at least 60 - 80 m²/g. Solomon does not disclose the requisite surface area of claim 19.

In view of the above, Applicant respectfully submits that all rejections and objections of record have been overcome and that the application is now in allowable form. An early notice of allowance is earnestly solicited and is believed to be fully warranted.

Respectfully submitted,



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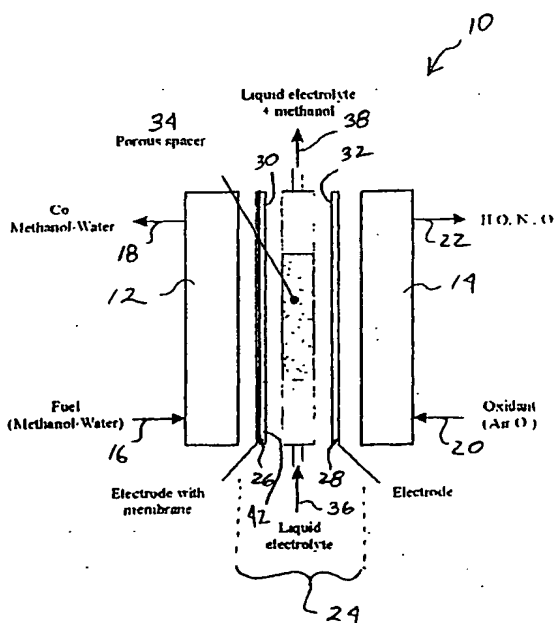
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(54) Title: DIRECT METHANOL CELL WITH CIRCULATING ELECTROLYTE



(57) Abstract: A fuel cell includes a circulating electrolyte for preventing fuel cross over.

WO 01/39307 A2

DIRECT METHANOL CELL WITH CIRCULATING ELECTROLYTE

BACKGROUND OF THE INVENTION

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1. FIELD OF THE INVENTION

The present invention relates to fuel cell systems and, more particularly, to fuel cell systems having reduced reactant cross-over.

10 2. DESCRIPTION OF THE PRIOR ART

Due to the increasing demands for inexpensive, efficient and non-polluting energy sources, various alternatives have been pursued. One of such alternative energy sources is the electrochemical fuel cell. Such fuel cells convert a generally commonly available fuel and an oxidant to electricity leaving relatively safe by-products. A typical fuel cell includes, 15 in addition to the fuel and oxidant, two generally planar electrodes (an anode and a cathode), and an electrolyte. Generally, the electrolyte is provided between the cathode and the anode. The electrodes are normally formed of a porous substrate that allows the fuel and oxidant to diffuse through and are usually covered on opposing surfaces with a catalyst for the respective reduction and oxidation (redox) reactions.

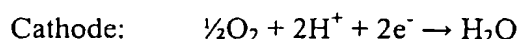
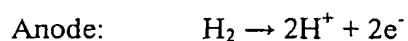
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The redox reactions result in the production of protons and electrons at the anode. The electrodes are electrically connected, through an external load, so as to provide a path for the electrons generated by the redox reactions. To accommodate the flow of protons from the anode to the cathode, the cells are normally provided with an ion, or more specifically, a proton exchange membrane between the electrodes.

25

In use, the fuel is passed through the porous anode substrate until it contacts the oxidation catalyst layer where it is oxidized. At the cathode, the oxidant diffuses through the porous cathode substrate and is reduced at the reduction catalyst layer. The fuels and oxidants for these cells are provided in a fluid state and consist of gases or liquids. Examples of fuels that can be used in fuel cells are hydrogen and lower alcohols such as methanol. The 30 oxidant is usually oxygen that can be supplied either as pure oxygen or as air.

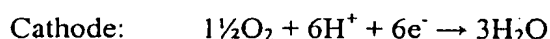
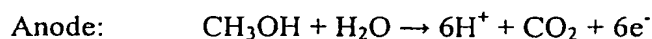
In the case of a hydrogen fuel cell, the fuel, hydrogen, is provided in a gaseous state and the following reactions take place:



As mentioned previously, the above oxidation reaction at the anode results in the production of protons and electrons. The electrons are conducted from the anode to the cathode by means of an electrical connection. The protons migrate from the anode to the cathode through the proton exchange membrane to react with the oxygen to form water.

Fuel cells can be categorized as "indirect" or "direct". In the case of indirect fuel cells, the fuel, usually a lower alcohol, is first processed, or reformed, before it is introduced into the cell. With direct fuel cells, the fuel is not pre-processed, thereby simplifying system.

In the case of a direct methanol fuel cell, the following reactions occur:



For the direct methanol fuel cell, the flow of protons and electrons are the same as that for the hydrogen fuel cell discussed above. The methanol fuel is provided in either a liquid or vapour state. It is known that other types of fuels may be utilized in such direct fuel cells. Such fuels may include, by way of example, other simple alcohols, such as ethanol, dimethoxymethane, trimethoxymethane, and formic acid. Further, the oxidant may be provided in the form of an organic fluid having a high oxygen concentration or hydrogen peroxide solution, for example. Such direct methanol fuel cells are taught in following US Patents: 5,672,439; 5,874,182; and, 5,958,616.

The electrolyte used in fuel cells may be either liquid or solid. In the case of a solid electrolyte, the proton exchange membrane may also serve as a polymer electrolyte membrane (PEM), thereby providing two functions. As taught in US Patent 5,958,616, such PEM's may comprise a hydrated sheet of a perfluorinated ion exchange membrane such as a polyperfluorosulfonic acid membrane, sold under the tradename NAFION® (E.I. du Pont de Nemours and Co.).

In any of the fuel cells mentioned above, it is important to maintain a separation between the anode and the cathode so as to prevent fuel from directly contacting the cathode and oxidizing thereon. For this reason, the proton exchange membrane must also function as a separator for the fuel and oxidant. However, the known membranes, although functioning well as proton exchangers and/or solid electrolytes, are not very efficient as fuel separators and a common problem in fuel cells is the incidence of fuel cross over, which occurs when

the fuel, prior to oxidation, diffuses through the membrane and contacts the cathode. Apart from the parasitic loss of fuel and oxidant from the system, such cross over results in a short circuit in the cell since the electrons resulting from the oxidation reaction do not follow the current path between the electrodes. Further, other disadvantages of fuel cross over may include structural changes on the cathode surface (i.e. sintering etc.) and poisoning of the reduction catalyst by fuel oxidation products.

One method of addressing this issue is to decrease the porosity of the membrane thereby preventing any fuel from crossing over. However, with this solution, the flow of proton will also be impeded, thereby resulting in decreased conductivity of the cell and, therefore, lower performance. As known in the art, fuel cell performance is defined as the voltage output from the cell at a given current density (or vice versa); thus, the higher the voltage at a given current density or the higher the current density at a given voltage, the better the performance.

The above mentioned US patents provide various solutions to the problem of fuel cross over in fuel cells. In each case, the solution provided lies in improvements to the PEM. For example, US Patents 5,672,439 and 5,874,182 teach novel PEM's having essentially a laminated structure wherein the PEM is provided with one or more layers of an oxidation catalyst for oxidizing any fuel that may diffuse through. US Patent 5,958,616 provides a PEM having a plurality of voids for sequestering any fuel that may be passing there-through. However, such membranes are more expensive thereby adding to the cost of the cell.

Another problem associated with PEM containing cells is that the membrane must be maintained in a hydrated state in order to function as a proton exchanger and as an electrolyte. This requires, therefore, a separate hydration system to ensure that the membrane does not dry out.

Thus, there exists a need for an improved fuel cell system that overcomes the above mentioned problem of fuel cross over as well as other deficiencies in the known systems.

SUMMARY OF THE INVENTION

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features of the preferred embodiments of the invention will become more apparent in the following detailed description in which reference is made to the appended drawings wherein:

5 Figure 1 is an exploded side cross sectional views of a direct methanol fuel cell according to one embodiment of the invention.

Figures 2 to 6 are side cross sectional views of a direct methanol fuel cell according to other embodiments of the invention.

10 Figure 7 is a schematic illustration of a direct methanol fuel cell system according to one embodiment of the invention.

Figure 8 is a graph illustrating the Open Current Voltage (OCV) of a fuel cell while in operation.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 In general terms, the present invention provides a fuel cell wherein any un-reacted fuel is purged from the system so as to reduce or eliminate any fuel cross over. As used herein, the term "fuel cross over" is intended to mean the un-desired flow of un-reacted fuel from the anode to the cathode.

20 In a preferred embodiment, the invention provides a fuel cell having a circulating electrolyte that flows between the electrodes (the anode and the cathode) of the cell and which serves to remove any un-oxidized fuel that diffuses through the anode. In this manner, un-reacted fuel is removed from the fuel cell before it reaches the cathode, thereby avoiding fuel cross over.

25 In one embodiment, the fuel cell of the invention allows any un-reacted fuel to be recycled back to the cell.

30 A direct methanol fuel cell according to one aspect of the invention is illustrated in Figure 1. As shown, the fuel cell 10 essentially consists of a planar "sandwich" having, as its outer surfaces, two end plates 12 and 14. The end plates may be formed as commonly known and may comprise materials such as polysulphon or other materials as will be known to persons skilled in the art. First end plate 12 is provided with a fuel inlet 16 and an outlet 18 for releasing un-reacted fuel and reaction products. Similarly, second end plate 14 is provided with an oxidant inlet 20 and an outlet 22 for un-reacted oxidant and reaction

products. The space between plates 12 and 14 essentially comprises the reaction chamber 24 of the fuel cell.

The reaction chamber 24 includes a pair of generally porous electrodes comprising an anode 26 and a cathode 28 having opposing surfaces 30 and 32, respectively. The electrodes
5 generally comprise sheets that are parallel to the plates 12 and 14. The electrodes may be made in any conventionally known manner and are formed of a porous material so as to allow the reactants to pass through. For example, electrodes for the present invention may be formed from a base of carbon cloth, or carbon fibre paper, having sprayed thereon, NAFION® and/or E-TEK. Other electrode materials will be apparent to persons skilled in
10 the art. For example, various porous carbon materials have been used to form electrodes for phosphoric acid fuel cells and such electrodes can be used, for example, in direct methanol fuel cells as well. Typically, the porous carbon electrodes are polytetrafluoroethylene (PTFE) bonded and have carbon sheets or carbon fleece as a base structure. Corrosion resistant stainless steel foams can also be used as an the base structure.

15 Although not shown in Figure 1, the electrodes are electrically connected as known in the art to conduct the flow of electrons generated in the cell.

Each of the opposing surfaces 30 and 32 of the electrodes are provided with a thin catalyst layer (not shown) for catalyzing the oxidation and reduction reactions of the cell. The catalysts that are used in the invention may be any of those commonly known such as
20 platinum (Pt), or a Pt and Ruthenium (Ru) combination. Various other catalysts for the fuel cell, such as carbon black, other noble metals etc., will be apparent to persons skilled in the art.

In the embodiment shown in Figure 1, the surface 30 of the anode 26 is provided with a proton exchange membrane 40. The membrane 40 preferably comprises a polymer
25 electrolyte membrane (PEM) as described above. In the preferred embodiment, the polymer electrolyte is acidic so as to act as an efficient hydrogen ion conductor and also to neutralize any CO₂ produced during the course of the reaction. In other embodiments, the membrane may be of any other commonly known material such as Gore-Tex® etc.

A medium 34 is provided between the electrodes 26 and 28, through which an
30 electrolyte is flowed. In one embodiment, as shown in Figure 1, the medium 34 comprises a porous spacer material positioned between the electrodes. The medium includes an electrolyte inlet 36 and an outlet 38 for the electrolyte and any reaction components entrained

therein. The electrolyte used in the preferred embodiment is an acidic solution and more preferably, comprises a solution of sulphuric acid.

In operation, the fuel is provided to the cell 10 via anode inlet 16 and, after the oxidation reaction, the resulting products and any un-reacted fuel is expelled from the system through outlet 18. Similarly, the oxidant for the reaction is introduced through cathode inlet 20 and the products from the reduction reaction are expelled through cathode outlet 22. The fuel diffuses through the porous anode 26 and is oxidized at the catalyst layer contained on anode surface 30. A proton exchange membrane 42 provided on surface 30 aids in conducting the protons towards the cathode. An electrical connection (not shown) conducts the electrons from the anode towards the cathode and through an external load. However, along with the protons generated by the oxidation reaction, a portion of any un-reacted fuel, and a portion of the reaction products may pass through the anode 26 and the membrane 42 and enter the medium 34 containing a fluid electrolyte stream (not shown). The electrolyte enters the medium via inlet 36 and exits at outlet 38. In passing through the medium 34, the electrolyte entrains any un-reacted fuel as well as any reaction products, such as CO₂. In this manner, the electrolyte stream contained in medium 34 removes any potentially damaging products and reactants from the fuel cell system thereby maintaining the performance of the cell. However, being acidic, the fluid electrolyte does not impede the flow of protons between the anode and the cathode.

Figure 2 illustrates another embodiment of the invention and shows the cell of Figure 1 in an assembled state and wherein like numerals are used to identify like elements. In the cell 10a Figure 2, the fluid electrolyte is not flowed through a medium but consists solely of an electrolyte stream. However, such cell functions in the same manner as the cell of Figure 1. Figure 2 also more clearly illustrates the electrical connection between the electrodes 26 and 28. Specifically, the anode 26 is connected to an external load 44 by means of a first conductor 46. Similarly, the load 44 is connected to the cathode 28 by a second conductor 48. Figure 2 also illustrates the use of a commonly known matrix 50 instead of an electrolyte membrane as in Figure 1.

Figure 3 illustrates yet another embodiment of the fuel cell of the invention, wherein elements common with Figure 1 are identified with like numerals. In the cell 10b of Figure 3, the anode 26 is provided with a PEM 42 as in Figure 1. However, in this case, the cathode 28 is also provided with a coating 52 comprising a Teflon® material. As illustrated, the cell

10b of Figure 3 includes a counter-current flow of oxidant with respect to fuel. The acid electrolyte follows the same direction as that of the fuel. The embodiment shown in Figure 3 also illustrates the use of a screen mesh 53 as the fluid electrolyte medium instead of the porous spacer 34 of Figure 1.

5 Figure 4 illustrates yet another embodiment of the fuel cell of the invention. In this case, the cell 10c is of a similar structure as that of Figure 3. As in Figure 1, the anode surface 30 is provided with a PEM. However, in this case, the cathode surface 54 facing the anode 26 is also provided with a PEM 56. As also illustrated in Figure 4, the medium through which the fluid electrolyte is passed comprises porous carbon material 58.

10 Figure 5 illustrates another embodiment of the invention wherein the cell 10d is generally of the same structure as that of Figure 4. However, in this case, the plate 12 of the anode side of the cell is not provided with outlet for the oxidation reaction products. Instead, such products, including and un-reacted fuel, is diverted to the fluid electrolyte stream and exits at a common outlet 60. Further the anode 62 of the cell of Figure 5 comprises a two-
15 phase electrode made of a porous carbon base and including fibre graphite and a Pt/Ru catalyst. As with Figure 4, the cathode is provided with a PEM 56.

 Figure 6 illustrates yet another embodiment wherein the cell 10e comprises generally the cell of Figure 5 with some modifications. Firstly, the cell 10e is provided with a fluid electrolyte medium that comprises a dual channel conduit 64, which serves to reduce fuel
20 cross over in two consecutive stages. Further, the anode 66 comprises another two phase structure comprising a gold plated screen with the desired catalyst.

 Figure 7 illustrates a schematic representation of the process of the invention. As can be seen, fresh fuel, which, in the embodiment illustrated is methanol, is provided to the system 100 at inlet 102. Fresh oxidant, such as air, is provided to the system at inlet 104.
25 The fuel is passed to a mixing tank 106, which will be discussed later, through an inlet 108. The outlet 110 of the mixing tank is fed to an inlet 112 of the cell 114. The cell 114 includes an outlet 116 for expelling the reaction products from the oxidation reaction. Such products are fed into a separator 118, which separates out any un-reacted fuel and diverts same to the mixing tank 106 where it is mixed with freshly supplied fuel. A vent 120 provided on the
30 separator 118 expels any reaction products (i.e. air, water, CO₂) from the system.

 In the cell, which is of any of the designs mentioned above, the fuel is oxidized to produce a proton and electron stream. The proton stream is diverted to the cathode where the

reduction reaction takes place. The electrons generated in the oxidation reaction are conducted from the anode to the cathode through an external load 111 via conductors 113 and 115. As discussed above, the invention provides the fuel cell with a circulating electrolyte to prevent any fuel cross over. As illustrated in Figure 7, the electrolyte is provided from a storage tank 122 and is fed into the cell via inlet 124. The flowing electrolyte collects any un-reacted fuel and other reaction products and exits the cell through outlet 126. The electrolyte stream is then fed to a separator 128, which separates the electrolyte from the reaction products and supplies re-generated electrolyte back to the storage tank 122. The separator also regenerates un-reacted fuel and returns same to the fresh fuel inlet stream.

Apart from above mentioned advantages, further advantages of the present invention include: improved cell heat dissipation; hydration of the PEM; removal of unwanted reaction products (e.g. CO₂). Further with the invention, any lost catalyst may also be recovered.

Examples

The following examples are used to illustrate the present invention and should not be considered to limit same in any way.

1. Manufacture of PEM:

For our investigations we used NAFION plus E-TEK electrodes (Single sided ELAT electrode 4 mg/cm² Pt/Ru). From the literature you get a very good idea of how to make own electrodes and how to prepare them properly. The base material often is a carbon cloth (35mm)[10] with Vulcan XC72 (30%PTFE, 20-30 µm) on both sides. As catalyst (30-40%PTFE) 20%Pt on Vulcan XC 72 diluted with XC72 is used. At the end NAFION solution is sprayed on the surface (M=1100kg/kmol, ~50A, 0-2,7 mg/cm² dry weight) which should diffuse for 10 min and dry for app. 2h at 80°C.

One major point concerns the preparation of NAFION. Before NAFION can be used several steps of preparation have been done namely boiling in

- 3% H₂O₂
- deionised water
- 0.5 M H₂SO₄
- deionised water

for over one hour each [10]. Afterwards the NAFION membranes have to be pre-dried (45 min. on a 60°C heated vacuum table. Then the catalyst layer has to be hot pressed onto the membrane at 125°C and 105atm for 120s [9] (140°C for 3 minutes [1]). The assembly has to be sandwiched between two uncatalysed carbon-cloth gas-diffusion backings (E-TEK). The parameters for pressing are

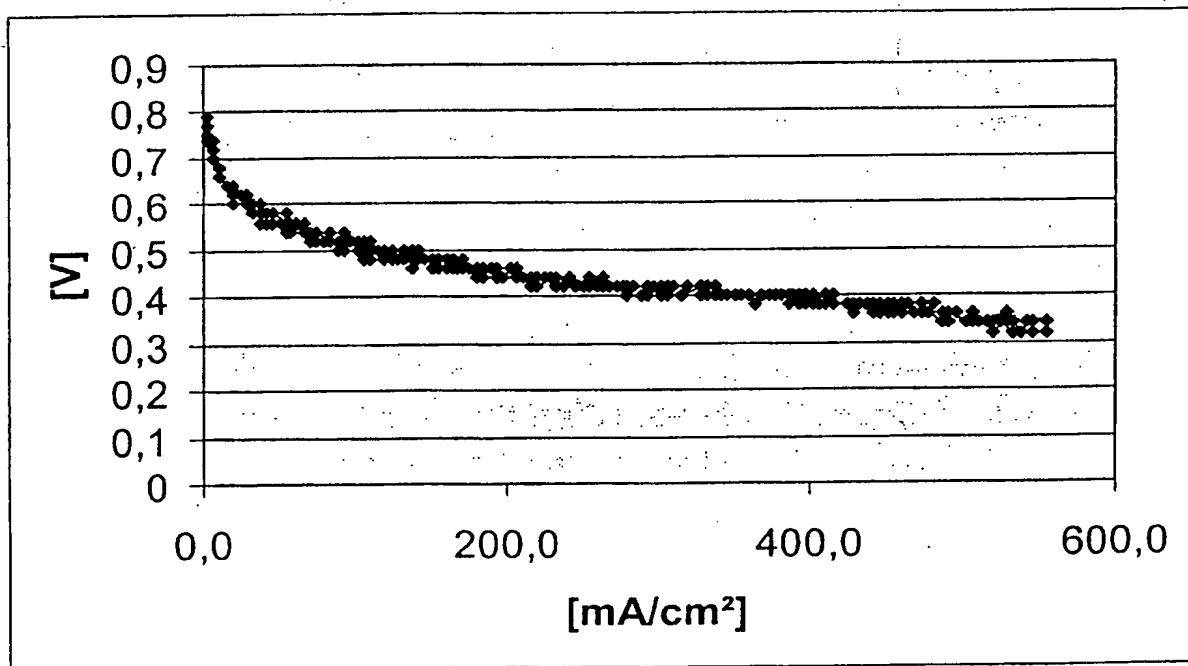
- temperature of app.140°C
- pressure of app.1000kg/cm²
- for 3min

2. Electrodes

The used electrodes have been ordered by E-TEK. The EFCG electrode on TGPH-120 Toray Carbon Paper has a loading of 4mg/cm² Pt/Ru. The ordered area is 23*23cm.

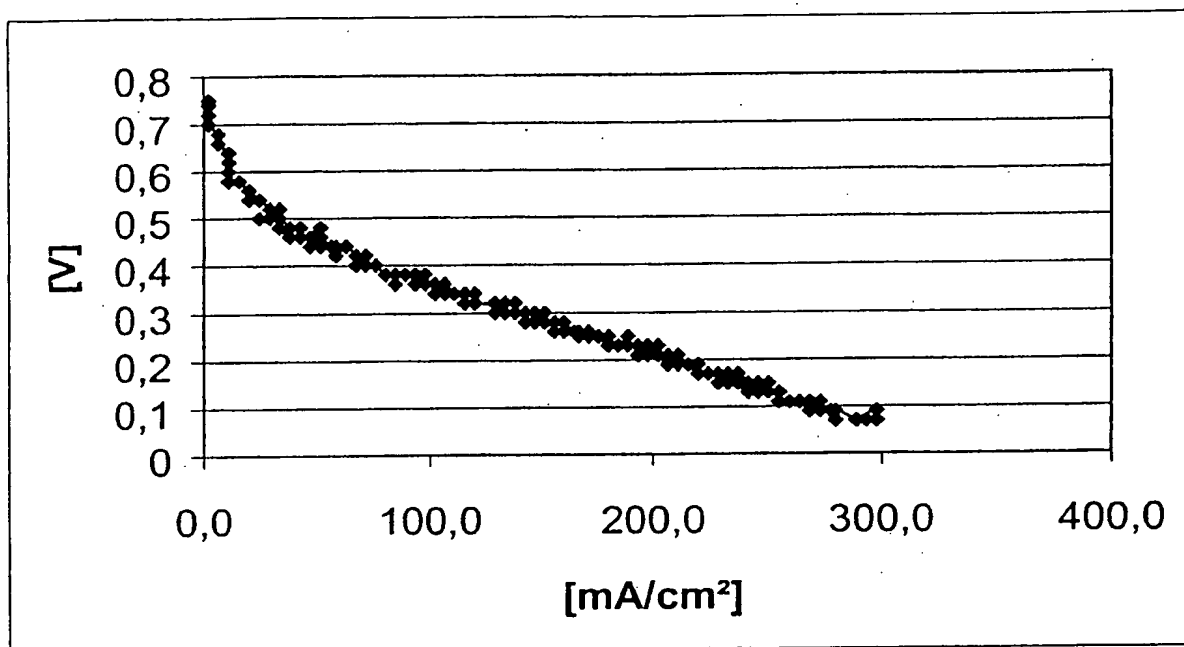
3. Test Results

The first built system ran with hydrogen and oxygen using a 0.5 M H₂SO₄ electrolyte between the anode and cathode. We did not heat the system up, so the temperature was app. 20°C. Graph 1 shows the recorded voltage/current-density curve. Because of our limited test equipment we were only able to go up to 2.5 A which corresponds to 550 mA/cm². This system works fine and provides 550 mA/cm² @ 0.35 V.



Graph 1: Voltage/Current density curve with hydrogen and oxygen at 20°C without pressure and 0.5 M H₂SO₄ as electrolyte.

- 5 The next step was to record U-I curves with the same system setup but air instead of pure oxygen. Graph 2 shows the graph and we reached only 300mA/cm² @ 0.1 V. The assumption is that a system running with air instead of pure oxygen has to be made pressurized.



- 10 **Graph 2:** Voltage/Current density curve with hydrogen and air at 20°C and pressure less

In order to have best conditions for first tests with methanol pure oxygen was used again. The system setup stays the same, but a new feeding system for methanol as fuel and for the circulating electrolyte has been introduced.

- 15 The first experiments did not lead to any promising results because there was a leakage problem at the anode side. The first used material (kind of neoprene) was too porous. So a special sealing gel (from the automotive sector) which is resistant against water alcohol solutions and high temperatures has been used. The good thing is that it remains plastic and therefore the cell can be opened again without any efforts. In order to avoid contact problems the O-ring sealing at the anode and cathode have been removed and this special sealing gel

has been used. This arrangement makes also sure that there is enough contact between the electrode and the carbon contact plate.

I measured the OCV which lied between 0.7 and 0.8. The recording of U-I curves failures because the cell voltage broke down under load.

5 The next step was to keep this system but to increase the temperature to 50,60, 90 °C. The results became better, always making first tests with a little fan. The problem is that it still was not possible to record curves because the voltage falls very rapidly under load (even when measuring resistance-free). Because of the boiling point at 64°C of methanol I stayed at a temperature of 60°C.

10 The change of the molarity of the electrolyte was the next step. So mixtures of 0.5, 1, 5 and 10 M H₂SO₄ have been tried out. The improvement was very little so the conclusion was that this influence is negligible.

Mixtures of 1, 2, 5 and 10 M MeOH I even put in pure methanol but I did not get improvements.

15 Because we are circulating the electrolyte it is possible to run with higher methanol concentrations.

20 The next step was to build a vapor feed system. We thought that the problem could be that no methanol comes to the fine pores when putting a load on the cell because those electrodes are gas diffusion electrodes. The temperature in the test rig was >90°C. We also did not get results because the OCV only reached app. 0.35 V and the cell did not even manage to power the fan.

All those experiments have been made without pressure and so the next step will be to build a system where the pressure can be changed.

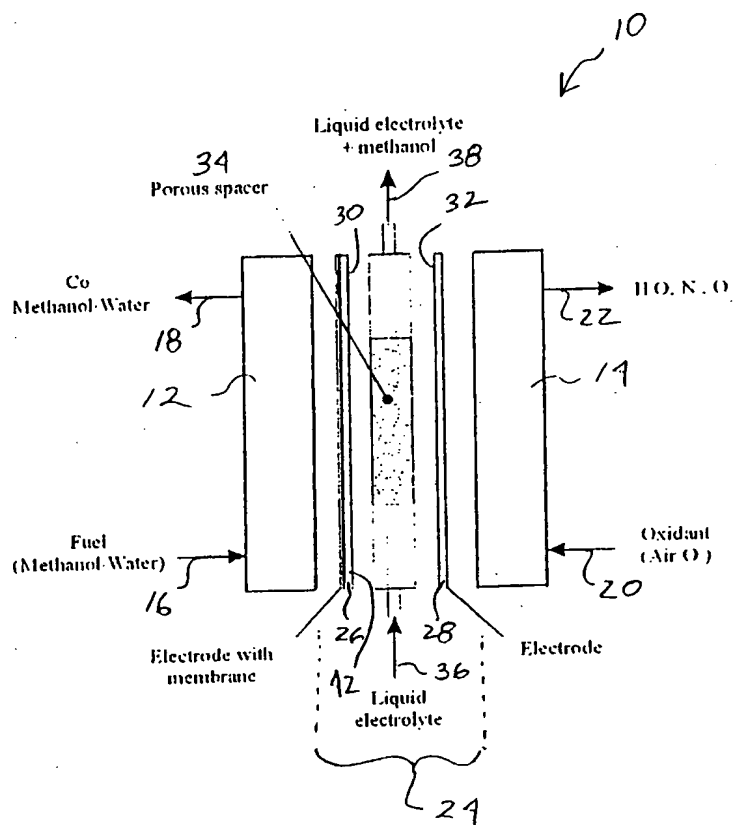
25 Although the invention has been described with reference to certain specific embodiments, various modifications thereof will be apparent to those skilled in the art without departing from the spirit and scope of the invention as outlined in the claims appended hereto.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A fuel cell system for the electrochemical production of electricity from liquid and gaseous fuels on the anodic side and oxygen and air on the cathodic side, whereby the electrode reactions are happening in catalyst regions (interfaces) contained in porous electrodes and the reaction products are continuously removed in circulating gas streams which also provide new gas supply and in a **circulating electrolyte** which serves also as a heat managing liquid stream, thereby characterized, that the speed of electrolyte circulation determines the build-up of the fuel or reactant cross-over gradient in the cell and the removed methanol is reclaimed in a distillation loop.
2. Fuel Cell System according to Claim 1, whereby separators or matrix may be attached to the electrodes to reduce the methanol outflow (at the anode) or minimize the reaction of the methanol on the air-cathode.
3. Matrix or separators according to Claim 2, where one of the separators (on the anode) can be of the PE-Membrane type.
4. The matrix or separator barriers according to Claim 2 may be chosen from microporous materials like asbestos.
5. In the system according to Claim 1, the circulating electrolyte is a good conductive salt solution selected from the group of battery electrolytes with a pH of neutral to low acidic values. Examples: KSCN or NH₄SCN, acidified K₂SO₄, or selected strong organic acids (Superacids).
6. Fuel Cell System according to Claim 1, whereby the temperature of the cell must be high enough to allow a methanol distillation recovery loop (over 70 deg.C.)
7. The fuel feed can be as an aqueous solution of methanol or as methanol vapor.

8. The fuel feed according to Claim 7 can be such that the concentration of the methanol (% in water or methanol gas vapor pressure) can be increased to give a higher anode voltage simultaneous with the adjustment of the methanol barriers and the speed of electrolyte circulation which reduce the crossover which will then tend to increase.
9. DMFC System according to Claim 1, whereby the electrodes can be porous all-carbon electrodes (the baked carbon type) in tubular or plate shape, carrying the proper catalysts for the anode and cathode reactions.
10. DMFC System according to Claim 1 where the electrodes can be of the type used for PAFC systems, sprayed or layered PTFE bonded porous carbon layers on a woven carbon (graphite) sheet or carbon fleece or carbon fiber carrier
11. Electrodes according to Claim 10 where the electrodes can be stainless steel screen supported plate (foil) structures layered with mixtures of activated carbon and suitable catalyst and fillers which are pore-formers (e.g. bicarbonates) or repellent binders (e.g. PTFE or PE.)
12. Electrodes according to Claim 11 whereby a CARBON/ PTFE/NAFION mix is used to produce the anodes of the DMFC, whereby the carrier is stainless steel wool.

Figure 1



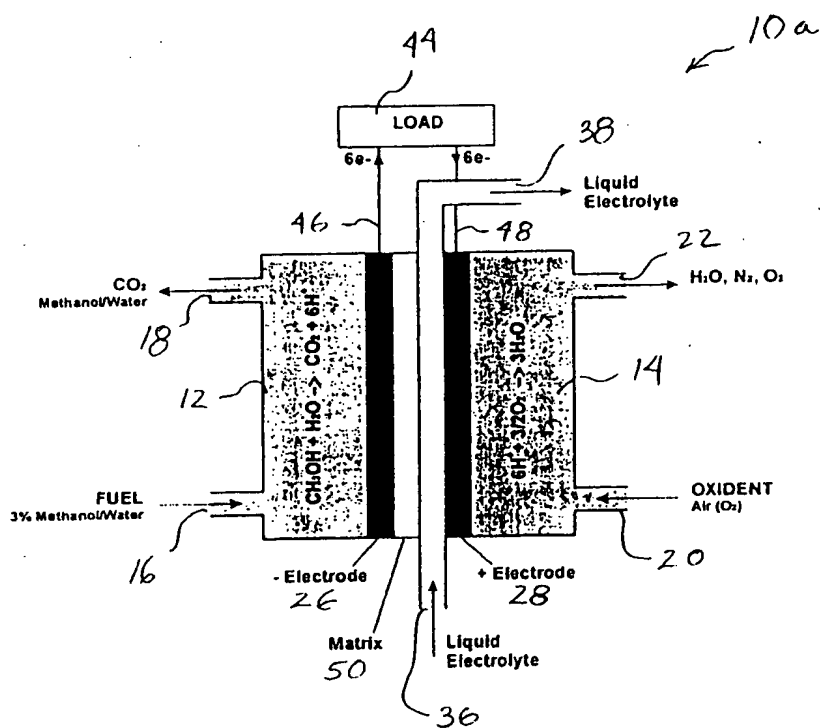


Figure 2

Figure 3

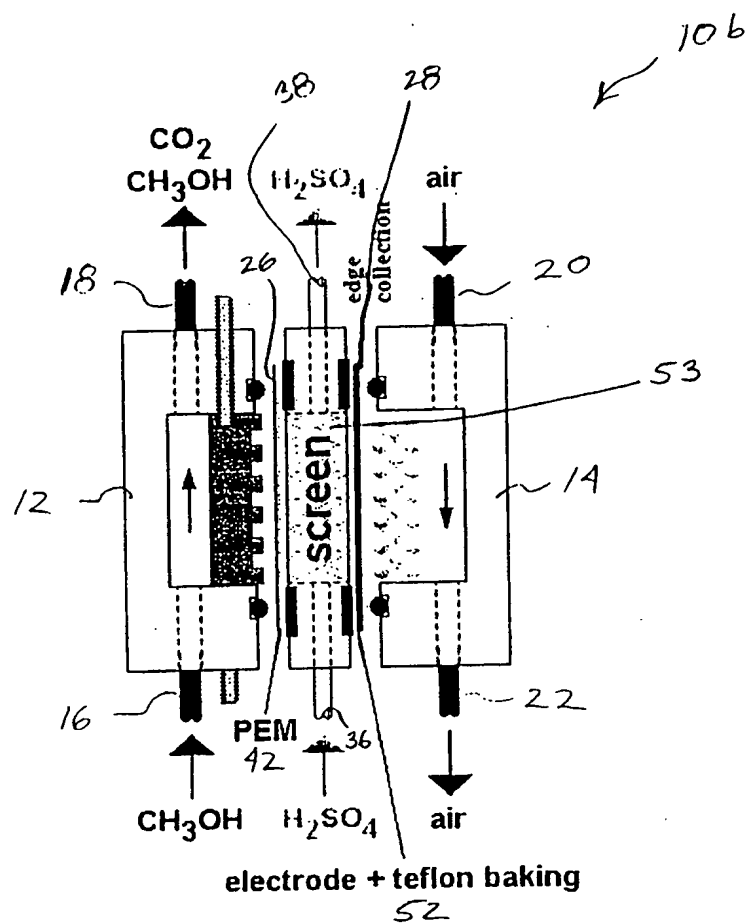


Figure 4

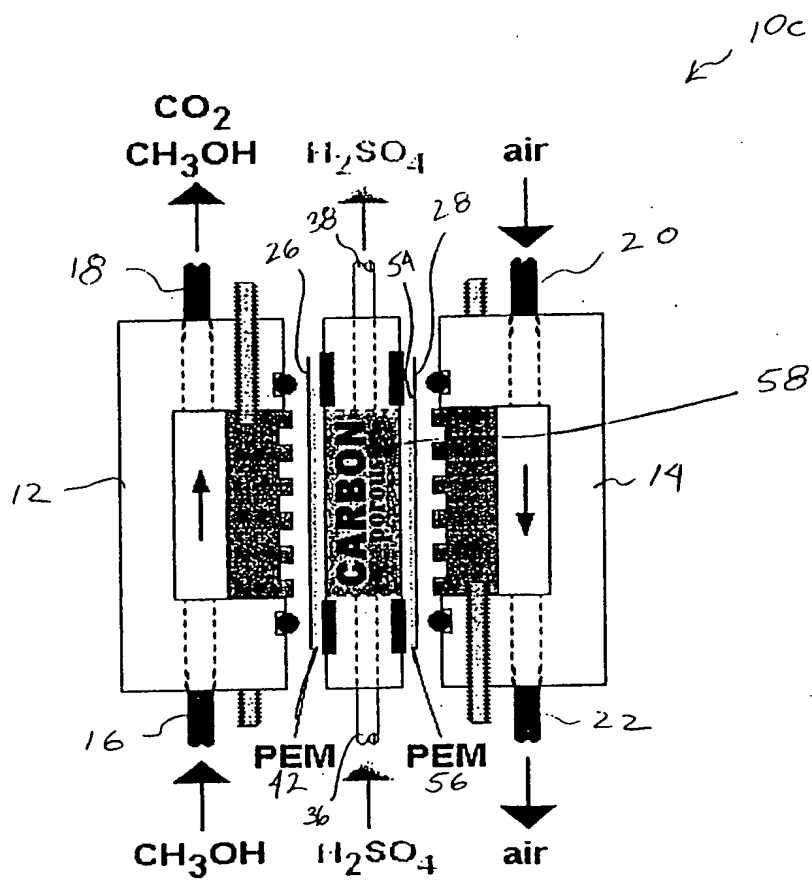


Figure 5

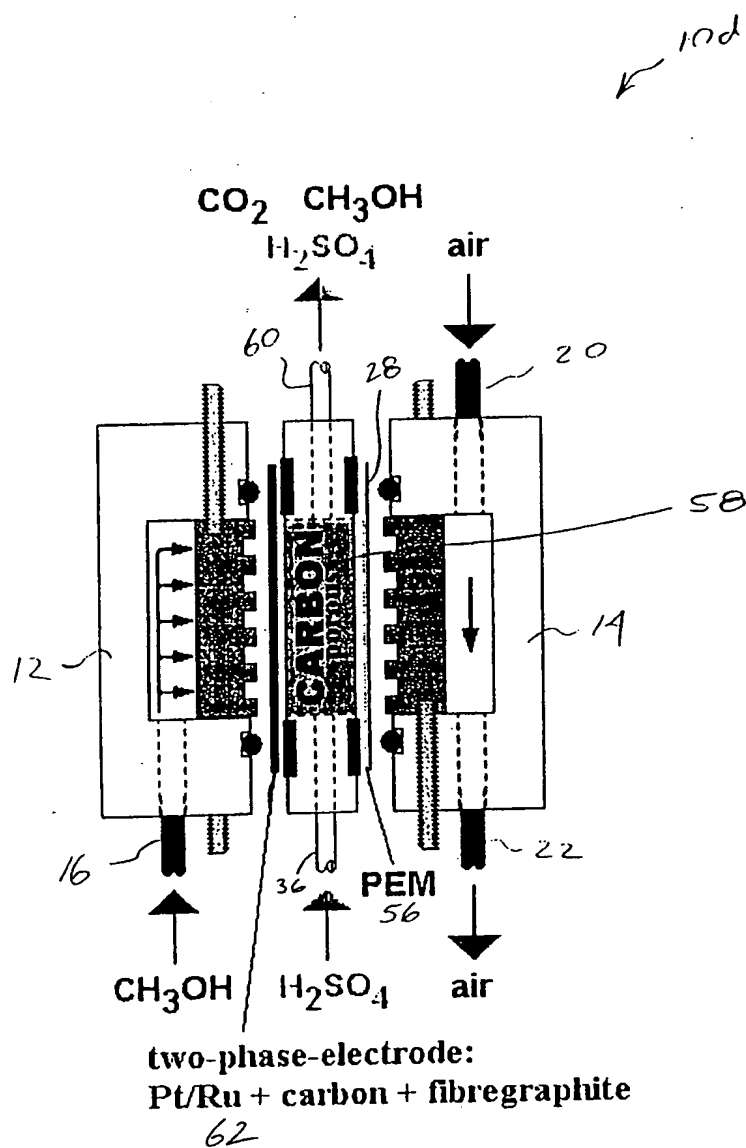


Figure 6

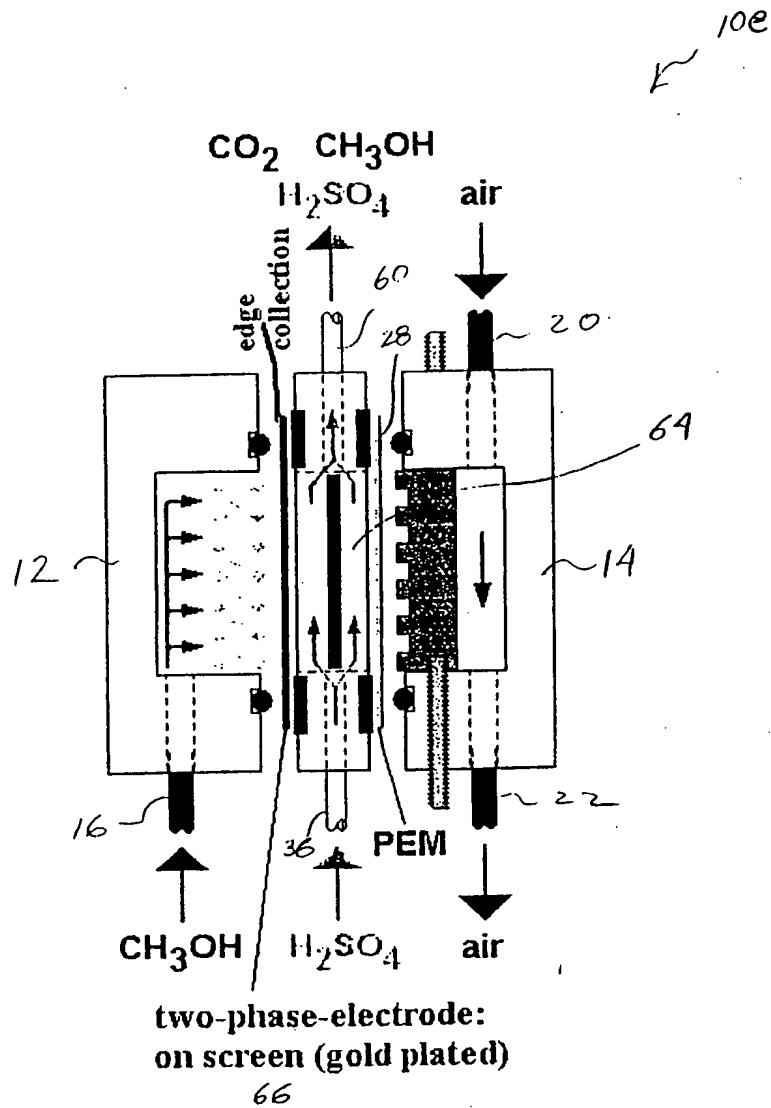


Figure 7

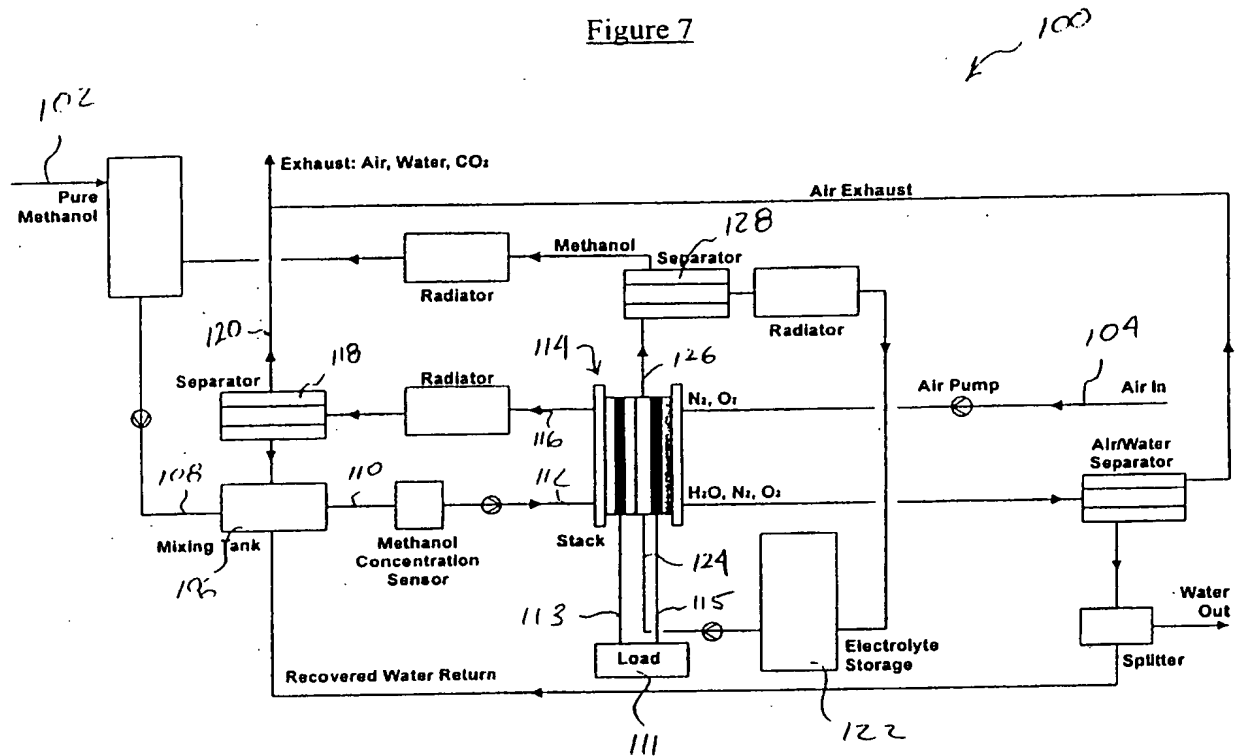


Figure 8

